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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*(54) Title: COMPOSITIONS FOR AND METHODS OF STABILIZING SUBTERRANEAN FORMATIONS CONTAINING
CLAYS(57) Abstract: A composition of matter for use in stabilizing shale formations in earth boreholes comprising polymeric products,
e.g., polymers of a dialkyl aminoalkyl methacrylate, which can optionally be quaternized with an alkyl halide to produce drilling
fluid additives which stabilize borehole formations containing reactive clays in the presence of an aqueous medium.

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COMPOSITIONS FOR AND METHODS OF STABILIZING SUBTERRANEAN FORMATIONS CONTAINING CLAYS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to polymeric compositions that can be used to stabilize reactive clays in subterranean formations and to a method of
5 stabilizing such reactive clays.

DESCRIPTION OF THE PRIOR ART

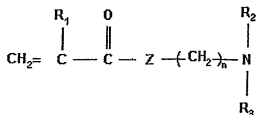
In the drilling of oil and gas wells and other such boreholes, it is generally necessary to use a drilling fluid that performs a variety of functions but is
10 primarily used to lubricate the drill bit and carry the cuttings to the surface. It is not uncommon to encounter formations during the drilling process that are argillaceous. These argillaceous formations contain clay (shale) particles, the proportion of which can vary over a wide range. When these argillaceous formations are encountered, and if a water based drilling fluid is employed,
15 complex chemical reactions take place within the argillaceous formation, including ion exchange, hydration, etc. These reactions result in swelling, crumbling or dispersion of the clay or shale particles in the formation through which the drill bit passes. Indeed, the problems can become so severe that washout and even complete collapse of the borehole can occur.

In an attempt to solve these problems, additives are included in the aqueous drilling fluid that are designed to arrest or slow down fluid invasion into the formation by forming an impermeable or semi-impermeable membrane on the surface of the borehole. For example, sodium silicate-based drilling fluids are believed to form such semi-impermeable membranes and are commonly used for maintaining shale stability. Other drilling fluid systems have also been used to deal with the problem of shale stabilization. For example, U.S. Patent No. 4,299,710 discloses a drilling fluid comprising an aqueous solution of a combination of thickeners such as a copolymer and a polysaccharide. Additionally, U.S. Patent No. 5,972,848 discloses a method for stabilizing shale formations by employing an aqueous solution containing a polymer with a hydrophilic group and a hydrophobic group.

SUMMARY OF THE INVENTION

In one preferred aspect, the present invention provides a composition of matter comprising a polymeric product selected from the group consisting of:

(1) polymers of a first monomeric component selected from the group consisting of (a) compounds having the formula:



wherein Z is oxygen or NH, R_1 is H or CH_3 , R_2 and R_3 are independently alkyl groups containing from 1 to 3 carbon atoms, and n is from 1 to 3, (b) quaternized compounds of Formula I obtained by reacting compounds of Formula I with an alkyl halide having the formula:



wherein R_4 is an alkyl group containing from 1 to 22 carbon atoms and X is a halide ion, and (c) mixtures of (a) and (b),

10 (2) polymers of compounds having the Formula I which have been polymerized and then quaternized with compounds having the Formula II,

 (3) polymeric mixtures of (1) and (2), and

 (4) polymers of compound (a) or (b) and a second monomeric component selected from the group consisting of (d) vinyl pyrrolidone (e)

15 compounds of the formula:



and mixtures of (d) and (e),

 (5) polymers of compounds (d) and (e) provided that Z is NH,

20 (6) polymeric mixtures of (1) and (4), and

 (7) polymeric mixtures of (2) and (4).

In another preferred aspect of the present invention, there is provided a method of stabilizing borehole formations containing reactive clays in the presence of water comprising contacting the formation with an aqueous medium

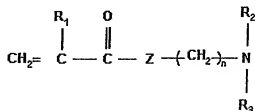
containing of a polymeric product as described above.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred form, the present invention involves hydrophobically
 5 modifying water-soluble polymers by adding water-insoluble groupings into the polymer to an extent that does not render the water-soluble polymer insoluble in water; i.e., its water solubility remains.

As can be seen from the formulas above, the composition of the present invention can take the form of a number of polymeric products which include:

10



15

wherein Z is oxygen or NH, R₁ is H or CH₃, R₂ and R₃ are independently alkyl groups containing from 1 to 3 carbon atoms, and n is from 1 to 3, (b) quaternized compounds of Formula I obtained by reacting compounds of Formula I with an alkyl halide having the formula:

20



II

wherein R₄ is an alkyl group containing from 1 to 22 carbon atoms and X is a halide ion, and (c) mixtures of (a) and (b),

(2) polymers of compounds having the Formula I which have been
 polymersized and then quaternized with compounds having the Formula II,

(3) polymeric mixtures of (1) and (2), and

(4) polymers of compound (a) or (b) and a second monomeric
 5 component selected from the group consisting of (d) vinyl pyrrolidone (e)
 compounds of the formula:



and mixtures of (d) and (e),

10 (5) polymers of compounds (d) and (e) provided that Z is NH,

(6) polymeric mixtures of (1) and (4), and

(7) polymeric mixtures of (2) and (4).

Compounds having the Formulas I and III can comprise an
 acrylic/methacrylic acid derivative, referred to herein generally as "acrylic acid
 15 derivative".

Generally speaking, when the first and second monomeric components
 are used to form a copolymer, the molar ratio of the first monomeric component
 to the second monomeric component will be from about 2:98 to 10:90.

The polymers of the present invention can be prepared by several
 20 methods. For example, if one desires to use a polymer of compounds having
 Formula I, a homopolymer can be made. Where first and second monomeric
 components are employed, one of the first monomeric components can be

reacted with one of the second monomeric components to produce a co-polymer of the first and second monomeric components. It will also be apparent that many other variations of preparing the compositions of the present invention can be employed. Thus, a co-polymer can be made from an acrylic acid derivative
5 having the structure of the Formula I and a quaternized version of the acrylic acid derivative having the structure of Formula I.

As can also be seen, polymer products obtained by mixing polymers described above can be employed. In yet another method, the acrylic acid derivative that has not been quaternized can be polymerized to form a polymer
10 of the desired molecular weight, following which it can be quaternized to the desired degree by reaction with the alkyl halide.

The molecular weight of the polymers of the present invention can vary over wide limits with molecular weights (wt. average) ranging from 50,000 to 500,000 being considered "low" molecular weight polymers, while copolymers
15 having molecular weights ranging from 500,000 to 5,000,000 being considered "high" molecular weight polymers.

The modified, i.e., quaternized polymers, of the present invention can be made by two methods:

Method 1

20 In this method, the acrylic acid derivative is reacted with the desired alkyl halide, which results in the alkyl halide attaching to the terminal nitrogen and quaternization of the nitrogen. This modified, quaternized monomer is isolated

and can then be copolymerized with more of the acrylic acid derivative, (Formula I), vinyl pyrrolidone, a compound of Formula III or a mixture thereof.

Method 2

5 In this method, the acrylic acid derivative, as described in Formula I, is homopolymerized, following which this polymer is reacted with a suitable alkyl halide in the presence of a surfactant. The surfactant is necessary because of the fact that the alkyl halide is not water soluble whereas the polymerized acrylic acid derivative is. Accordingly, the surfactant acts to solubilize the alkyl halide
10 such that it can react with the terminal nitrogen of the acrylic acid derivative.

The polymers of the present invention have been shown in laboratory testing to vastly reduce shale erosion. A shale erosion test is commonly employed to determine the ability of a drilling fluid and/or the additives therein to prevent a shale from eroding in the presence of an aqueous medium such as
15 an aqueous based drilling fluid. Such erosion, when encountered in actual field conditions in a borehole, and as noted above, can lead to problems ranging from a washout to a complete collapse of the borehole.

A typical shale erosion test is conducted by rolling a weighed portion of sized shale particles in an aqueous medium and then screening the particles to
20 determine the amount of shale that eroded to the point of passing through a selected sized screen. In the shale erosion test used with the compositions of the present invention, U.S. Standard Sieve Series No. 6 and No. 14 screens

were employed. The shale was crushed and ground into particles that passed through the 6 mesh screen but were retained on the 14 mesh screen; i.e., particles of a size (-6+14) were used for the erosion test. Equal portions (40.00 g) of the shale were put into one laboratory barrel (350 ml) of each of the various
5 test drilling fluids and rolled at 150°F for 16 hours. The drilling fluids were then screened through the 14 mesh screen and the retained solids were washed, dried, and weighed. The percent of erosion was calculated based on the weight loss, corrected for the moisture content (7.67%) of the original sample.

The composition of the present invention can be used in fluid for treating
10 subterranean formations including, but not limited to, drilling fluids, completion fluids, remedial fluids and the like. In the method according to the present invention, a drilling fluid containing one of the compositions described above would be incorporated in a suitable amount, e.g., from 1 to 20 lbs/bbl, in the drilling mud or fluid, which, in the conventional fashion, would be circulated in the
15 borehole during the drilling operation. If, during the drilling operation, a formation were encountered that contained a reactive clay, e.g., a clay that had a tendency to erode in the presence of water, the presence of the polymer compositions of the present invention would stabilize the shale, minimizing or ideally stopping the erosion. It is also to be understood that in addition to
20 incorporating the compositions of the present invention in drilling fluids or muds, it can be also used in other downhole fluids under certain circumstances when it is desired to stabilize shale formations.

To more fully illustrate the present invention, the following non-limiting examples are presented:

Example 1

A series of polymers was prepared according to Method 1 described
5 above. To prepare a quaternized monomer of Formula I, to a 100 mL round
bottom flask is added 16.7 grams of dimethylaminoethyl methacrylate (DMEMA)
and 16.2 grams of hexadecyl bromide. The mixture is heated to 110° F and
stirred for 24 hours. The mixture is then poured into 1 liter of petroleum ether,
resulting in precipitation of the quaternized monomer. The monomer is collected
10 on a Buchner funnel, washed with excess petroleum ether, collected, and dried
in a vacuum dessicator.

To prepare a copolymer, to a 250 ml round bottom flask charge the
following: 3.8 grams of DMEMA, 0.7 grams of the quaternized monomer
described above, 84.5 grams water, and 1.2 grams concentrated sulfuric acid
15 (to achieve a pH of ~7.1). This solution is then sparged with nitrogen for 30
minutes, followed by the addition of 0.035 grams 2,2'-azobis (2-amidinopropane)
dihydrochloride. The resulting solution is then heated under a nitrogen
atmosphere, with stirring, to 110°F and held for 18 hours to produce a highly
viscous polymer solution. In all of the test samples in this example, the acrylic
20 acid derivative employed was DMEMA. The alkyl halide employed was an alkyl
bromide, the carbon number appearing in the column labeled "Monomeric
Component 1" referring to the chain length of the alkyl group. Except as

otherwise indicated, each sample contained 1% by weight of the polymer in deionized water. The results are shown in Table 1 below.

Table 1

Sample	Monomeric ³ Component 1 (Mole %)	Monomeric Component 2	Relative Molecular Weight	% Erosion
1	-	DMEMA	High	17
2 ¹	6% C ₁₀	"	"	7
3	"	"	"	0
4	10% C ₁₆	"	"	1
5	15% C ₁₆	"	"	-1
6	20% C ₁₆	"	"	-1
7	30% C ₁₆	"	"	11
8 ²	4% C ₁₈	"	"	7
9	-	"	Low	10
10	6% C ₁₆	"	"	17
11	15% C ₁₆	"	"	18

¹2.3 wt. % polymer in water.

²1.6 wt. % polymer in water.

³Molar percent of quaternized DMEMA in copolymer.

Example 2

In this example, the polymers were also prepared according to the procedure of Method 1 as described above with respect to Example 1. In all cases, the acrylic acid derivative employed was DMEMA, and, unless indicated otherwise, each sample contained 1% by weight of the polymer in deionized water. The results are shown in Table 2 below.

Table 2

Sample	Monomeric ² Component 1 (Mole %)	Monomeric Component 2	Relative Molecular Weight	% Erosion
1	-	VP	High	33
2	6% C ₁₆	"	"	2
3	"	"	Low	44
4	10% C ₁₆	"	"	16
5	20% C ₁₆	"	-	4.6

10 ¹Vinyl pyrrolidone.

²Molar percent of quaternized DMEMA as per Formula III in copolymer.

Example 3

In this example, a copolymer was prepared according to Method 2
 15 described above. A homopolymer of DMEMA is prepared as follows. To a 3 L
 round bottom flask is added 1968.0 grams of water, and this is sparged with
 nitrogen for 1.5 hours. Next is added 105.0 grams of DMEMA, 25.8 grams
 concentrated sulfuric acid (to achieve a pH of ~7.9) and 0.46 grams 2,2'-azobis
 (2-amidinopropane) dihydrochloride. The mixture is then heated under a
 20 nitrogen atmosphere, with stirring, to 110°F and held for 18 hours to produce
 a highly viscous polymer solution.

The copolymer is produced as follows. To a 250 mL round bottom flask
 is added 71.0 grams of the DMEMA homopolymer, as described above, followed
 by 4.0 grams 15% NaOH (to achieve a pH of ~8.9). Next is added 54.6 grams
 25 water, 0.36 grams hexadecyl bromide and 0.39 grams

benzylcetyldimethylammonium bromide. This mixture is then heated, with stirring, to 140°F for 24 hours.

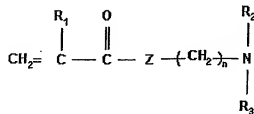
The copolymer produced contained 6% (molar) of hexadecyl bromide and was of high molecular weight. A 1% by weight solution of the polymer in
5 delonized water exhibited 0% erosion.

As can be seen from Table 1, a homopolymer of DMEMA which has not been quaternized exhibits some degree of erosion control. It has also been found that a homopolymer of DMEMA subsequently quaternized with hexadecyl bromide and of high molecular weight exhibits a -2% erosion. The foregoing
10 description and examples illustrate selected embodiments of the present invention. In light thereof, variations and modifications will be suggested to one skilled in the art, all of which are in the spirit and purview of this invention.

CLAIMS

A composition of matter comprising a polymeric product selected from the group consisting of:

5



10 wherein Z is oxygen or NH, R₁ is H or CH₃, R₂ and R₃ are independently alkyl groups containing from 1 to 3 carbon atoms, and n is from 1 to 3, (b) quaternized compounds of Formula I obtained by reacting compounds of Formula I with an alkyl halide having the formula:

15



II

wherein R₄ is an alkyl group containing from 1 to 22 carbon atoms and X is a halide ion, and (c) mixtures of (a) and (b),

(2) polymers of compounds having the Formula I which have
20 been polymersized and then quaternized with compounds having the Formula II,

(3) polymeric mixtures of (1) and (2), and

(4) polymers of compound (a) or (b) and a second monomeric

component selected from the group consisting of (d) vinyl pyrrolidone (e) compounds of the formula:



5

and mixtures of (d) and (e),

- (5) polymers of compounds (d) and (e) provided that Z is NH,
- (6) polymeric mixtures of (1) and (4), and
- (7) polymeric mixtures of (2) and (4).

10

2. The composition of Claim 1 wherein said first monomeric component comprises quaternized dimethylaminoethyl methacrylate.

3. The composition of Claim 1 wherein said first monomeric
15 component comprises dimethylaminoethyl methacrylate.

4. The composition of Claim 1 wherein said second monomeric component comprises vinyl pyrrolidone.

20 5. The composition of Claim 1 wherein said second monomeric component comprises compounds having the Formula III.

6. The composition of Claim 1 wherein said first monomeric component and said second monomeric component are in a molar ratio of from 2 :98 to 10:90, respectively.

5 7. The composition of Claim 1 wherein said alkyl halide comprises an alkyl bromide.

8. A method of stabilizing borehole formations containing reactive clays in the presence of water comprising:

10 contacting said formation with an aqueous medium comprising a composition according to any one of Claims 1-7.

9. A fluid for use in borehole operations comprising an aqueous medium and an effective amount of a composition according to any one of
15 Claims 1-7.

10. A method of treating a subterranean formation comprising:
contacting said formation with a fluid comprising a composition according
to any one of Claims 1-7.

INTERNATIONAL SEARCH REPORT

PCT/GB 03/02953

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K7/02 C09K7/00 E21B43/25 C08F220/34 C08F220/60
C08F220/56 C08F226/10 C08L33/14 C08L33/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K E21B C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 221 940 A (BAROID TECHNOLOGY INC) 21 February 1990 (1990-02-21) abstract; claims	1-3, 5, 6, 9, 10
X	US 4 699 722 A (DYMOND BRIAN ET AL) 13 October 1987 (1987-10-13) the whole document	1, 4-6, 9, 10
X	US 5 342 530 A (AFTEN CARL W ET AL) 30 August 1994 (1994-08-30) column 3; claims 1, 5, 12, 14	1-3, 6, 8-10
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"Z" document member of the same patent family

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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